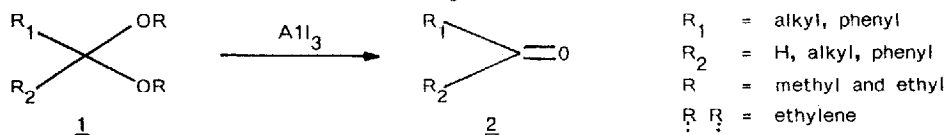


A FACILE PROCEDURE FOR SELECTIVE CONVERSION OF KETALS TO CARBONYL COMPOUNDS

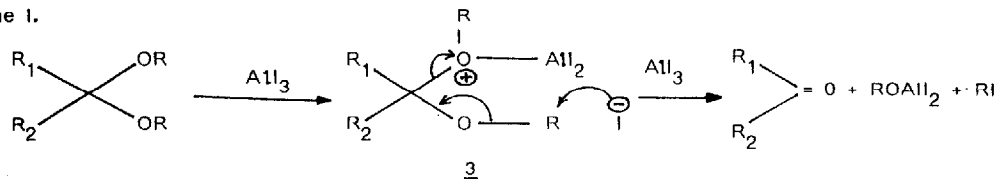
Parijat Sarmah and Nabin C. Barua*
Division of Natural Products Chemistry,
Regional Research Laboratory, Jorhat 785 006, Assam, INDIA

Summary Ketals are selectively cleaved by aluminium triiodide (AlI_3) to the corresponding carbonyl compounds in excellent yields. However, thioketals are not affected by this reagent.

The conversion of ketals and thioketals to the corresponding carbonyl compounds constitutes an important part of the organic synthetic transformations. Numerous methods are reported in the literature¹ for such conversions, but paucity is always felt by synthetic chemists for methods of selective deprotection of either ketals or thioketals. Besides, most of the existing procedures for such conversion involve aqueous reaction conditions and therefore may not always be applicable to substrates containing water sensitive functionalities. Reports of non-aqueous cleavage of ketals or thioketals are also scanty in the literature. The procedure reported by Liu et al.² using a combination of phenyl dichlorophosphate/DMF and NaI is selective for thioketals and Jung et al.³ used iodotrimethylsilane for selectively cleaving ketals in good yields. In this letter we wish to report a simple procedure for selective cleavage of ketals to carbonyl compounds using freshly prepared AlI_3 .⁴



Recent investigations have shown AlI_3 to be a useful reagent for affecting a variety of synthetic transformations⁵⁻¹⁰. In continuation of our study on the utility of this reagent, we observed that AlI_3 has a greater affinity towards etheral oxygen and forms a mild complex with it through aluminium. We argued that ketals on treatment with this reagent in an aprotic solvent would form a complex of the type 3 and release the parent carbonyl compound according to the electronic rearrangement shown in scheme 1.



Our surmise was indeed proved to be correct when several of the acetals and ketals listed in Table 1 reacted with AlI_3 to furnish the parent carbonyl compounds in good to excellent yields.

It is noteworthy that thioketals remain unaffected under these conditions.

The alternative non-aqueous selective deprotection procedure described above for ketals will certainly make a useful alternative to the existing procedures.

General procedure : To a solution of the substrate (0.3 mmol) in acetonitrile¹¹ (6 ml) is added a freshly prepared pale yellow solution of AlI_3 in dry benzene (1 ml, 35 mmol) with continuous stirring at r.t. while monitoring the reaction on TLC. For work up the reaction mixture is poured into cold water, extracted with CHCl_3 (3x50 ml), washed with 10% aqueous sodium thiosulfate solution, dried over Na_2SO_4 and evaporated under reduced pressure. The products are purified by chromatography or by distillation.

Table 1 Conversion of acetals and ketals to carbonyl compounds

Entry	Substrate ^a	Reaction Time (min)	Product ^b	Yield ^c (%)
1	Acetophenone diethyl ketal	10	Acetophenone ^d	86
2	Cyclohexanone diethyl ketal	10	Cyclohexanone	90
3	Benzaldehyde diethyl acetal	10	Benzaldehyde ^d	80
4	Ethyl methyl ketone ethylene ketal	15	Ethyl methyl ketone	70
5	Benzaldehyde ethylene acetal	10	Benzaldehyde ^d	82
6	Acetophenone ethylene ketal	30	Acetophenone ^d	83
7	16-Dehydro-pregnenolone acetate ethylene ketal	15	16-DPA	85
8	Δ^5 -cholesten-3-one ethylene ketal	5	Δ^4 -Cholestenone ^e	92
9	Δ^4 -Cholesten-3-one ethylene ketal	5	Δ^4 -Cholestenone	90

(a) All the substrates mentioned in Table 1 are prepared following standard literature procedures and are purified before use. (b) Products are characterised by IR, NMR, MS and by direct comparison with the authentic compounds (c) Yield in entries 7,8 & 9 refers to yields of pure isolated products and in case of entries 1 to 6 yields are determined by GLC. (d) Use of excess reagent leads to the formation of a less polar product and hence, it is recommended to use slightly less than one equivalent of the reagent in these cases. (e) The 5,6 double bond rearranges to the 4,5 position during the reaction.

Acknowledgement : Authors are grateful to Dr R.P. Sharma for helpful discussions and Director, RRL-Jorhat for providing necessary facilities.

References & Notes :

- Greene, T.W., "Protective Groups in Organic Synthesis" John Wiley and Sons, New York, 1981, pp. 129-138.
- Liu, H.J., Wiazewski V. Tetrahedron Letters, 1988, **29**(43), pp. 5471-5474 and references cited therein.
- Jung, M.E., Andrus, A.W., Ornstein, P.L., Tetrahedron Letters, 1977, (48), pp. 4175-4178 and references cited therein.
- Anderson, S., Synthesis, 1985, 437-439.
- Bhatt, M.V., Babu, J.R., Tetrahedron Letters, 1984, **25**, 3497-3500.
- Babu, J.R., Bhatt, M.V., Tetrahedron Letters, 1986, **27**, 1073-1074.
- Kline, E.R., Compbell, B.N., Jr., Spaeth, E.C., J. Org. Chem., 1959, **24**, 1781-1783.
- Broome, J., Brown, B.R., Summers, G.H.R., J. Chem. Soc., 1957, 2071-2073.
- Sarmah, P., Barua, N.C., Tetrahedron Letters, 1988, **29**, 5815-5816.
- Sarmah, P., Barua, N.C., Tetrahedron, 1989, **45**, 3569-3574.
- Some amount of dry CH_2Cl_2 is also added in case of substrates less soluble in Acetonitrile.

(Received in UK 13 July 1989)